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JOURNAL

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EIGHTEENTH YEAR—PART FIRST

1901

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.[1]

CHARLES BASKERVILLE.

Almost five years ago I attempted to separate thorium quantitively from a neutral chloride solution by saturation with sulphur dioxide and boiling. As may be recalled, this was merely an application of the method formerly made known by me and used in the separation of zirconium[2] and titanium.[3] The separation of thorium by this method was not quantitive. On resolution of the precipitated portion in hydrochloric acid and exact neutralization with ammonium hydroxide and treatment again with sulphur dioxide, almost complete precipitation resulted, showing that the initial partial precipitation was not altogether due to imperfect action of the precipitant or the solubility of the basic thorium sulphite[4] in the neutral menstruum. This was verified by many

1 Presented at the Denver meeting of the American Chemical Society.

2 *Chem. News*, 70, 57, (1894); *J. Am. Ch. Soc.*, 16, 475 (1894).

3 *J. Am. Chem. Soc.*, 16, 473 (1894).

4 These basic sulphites are being investigated at present. It may be well to state that in addition to a flocculent basic sulphite there has been obtained a gelatinous compound, or hydrogele, similar in appearance to the zirconium sulphite described by Venable and Baskerville, *J. Am. Chem. Soc.*, 17, 448 (1895).

repititons of the process using thorium chloride solutions of different strengths and varying amounts of ammonium chloride.

These solutions were first made upon fairly pure thorium salts prepared by me from oxides obtained from analyses of many monazite sands for the North Carolina Geological Survey.[1] As this conduct was unexpected and not in keeping with the observed reactions of the group, the experiments were repeated with thorium compounds obtained from different sources with like results. I was favored with several grams of thorium sulphate prepared by Professor Dunnington, of Virginia, from monazite sand found in Amelia County (Va). Prof. Dennis, of Cornell, kindly gave me 3.5 grams thorium nitrate (99.6 per cent. pure). The hydroxide from which it had been prepared was separated by means of potassium hydronitrate.[2] I worked up about 5,000 liters of thorium sulphate solution obtained from Carolina monazite kindly collected by the late Mr. H. B. C. Nitz, assistant state geologist. The procedure followed need not be detailed here, as it will appear in a subsequent and more extended communication. Finally, Dr. Waldron Shapleigh generously gave me 2 kilograms of the purest thorium oxalate to be had at the Auer Welsbach works. My thanks are due these gentlemen for their kindness.[3]

1 Bulletin 9, "Monazite and Monazite Deposits in N. C.," 1895.

2 *J. Am. Chem. Soc.*, 18, 947 (1896).

3 While in the midst of repurifying the compounds from such varied sources and desiring to leave no stone unturned in the ivestigation, during the fall of last year I wrote Prof. Bohuslav Brauner, of Prague, of my observations and requested a small amount of the purified thorium compound used by him in his excellent work on the atomic weight of that element [*J. Chem. Soc.* London (Trans.), 73, 951 (1898).] Very likely the letter went astray as I have received no reply. I was surprised, therefore, to observe in the proceedings of the London Chemical Society (April 10, 1901), an article by him on "Contributions to the Chemistry of Thorium," in which he gives good evidence of the complexity of thorium, dividing that element into Th(a) and Th(b). Immediately at my first opportunity (April 23), at the meeting of the N. C. Section of the American Chemical Society, I made public mention of my work, which had been discussed often in private with others. Brauner's results were obtained by hydrolysis of the heptahydrated thorium tetrammonium oxalate. This communication contains

The purest thorium compounds were repurified by the following procedure: The sulphate was taken up in cold water, treated with sodium sulphate and allowed to stand from twelve to twenty-four hours to insure separation of the remaining cerium salts, the percentage of which was quite small. The liquid was filtered and the hydroxide precipitated in tall cylinders by a large excess of chemically pure sodium nitrite. This precipitate was washed by decantation from six to ten times, using 20 volumes (to 1 of precipitate) of distilled water each time. To remove the last of the sodium salts and other soluble impurities the precipitate was then dissolved in hyhrochloric acid reprecipitated by slight excess of ammonium hydroxide and washed by decantation at least ten times, using 20 volumes of distilled water.

1. VARIATION IN THE SPECIFIC GRAVITY OF THE OXIDE.

The determination of the specific gravity of the oxides affords a rapid and excellent means of judging the rate of fractionation and in a measure the purity of the rare earths. This method has been especially urged independently by Muthmann and Bohm[1] as having time advantages over the necessarily long and ofter tedious equivalent determinations. Brauner also uses the method. The oxide obtained by prolonged ignition with the blast of the purified hydroxide obtained above had a specific gravity of 10.1 corrected 4° C. Clarke,[2] in his "Constants of Nature," gives the following values:

in part the results of my experiments reported then and some observations made since. As soon as the unexpected properties were noted almost five years ago, I indicated the differences by terming one Th and the other Th(X). It is deemed well to make this explanation in presenting a preliminary paper on incomplete work, as it was done independently and the problem was attacked in a different way. Results have been obtained which corroborate Brauner's work. It may also be stated that large quantities of the materials are being worked up and the work will be pushed to a finality.

1 *Ber. d. Chem. Ges.*, 33, No. 1; *Chem. News*, 81, 181.

2 Smithsonian Institution, Part I, p 48 (1868).

Name and formula.		sp. gr.	Authority.
Thorium dioxide, ThO_2.		9.402	Berzelius.[1]
		9.21	Nordonskjöld and Chydenius.[2]
		9.077	Chydenius.[3]
		9.200	
		9.861	Nilson and Petterson.[4]
	17°	10.2199	Nilson.[5]
		10.2206[6]	
	15°	9.8767	Troost and Ouvrard.[8]

About 10 grams of the purified hydroxide obtained above were dissolved in hydrochloric acid, made up about 300 cc., and exactly neutralized by dilute ammonium hydroxide. To insure neutrality, the ammonia was added until the slightest permanent precipitate remained after stirring the cold solution vigorously for five minutes. The precipitate was separated by filtration and the solution saturated with freshly prepared and washed sulphur oxide. Within a few minutes a flocculent basic sulphite began to separtae. As the reaction continued in the cold the precipitate increased and then decreased somewhat. The solution was filtered cold and the filtrate boiled giving a second but much smaller precipitate similar to the first, showing that the precipitate is soluble to some extent in the cold sulphurous acid solution. The hot filtrate was then precipitated with a slight excess of ammonium hydroxide and filtered off. Portions of the sulphite and ammonia precipitates were removed from the funnels, care being taken that they were not contaminated with ashless filter-paper, ignited in platinum crucibles with the blast and the specific gravity of the oxides determined.

1 Pogg. *Ann.*, 16, 385.
2 *Jsb. Chem.*, 13, 134.
3 *Ibid.*, 16, 194.
4 *Compt Rend.*, 91, 232.
5 *Ber. d. chem. Ges.*, 15, 2336.
6 Reduced to 4° C., this value is 10.201.
7 Clarke gives a note stating that Nilson's determination is the only one of value.
8 *Compt. Rend.*, 102, 1422.

Before treatment.	Sulphur dioxide precipitate.	Soluble portion precipitated by ammonia.
10.1	9.38	10.367[1]

Twenty grams of Shapleigh's purest thorium oxalate were repurified according to the method given above. A saturated solution of chemically pure citric acid was prepared and the pure hydroxide added in excess; *i. e.*, until no more was dissolved cold when the stirring had continued (by means of a motor) for from twelve to fifteen hours (different experiments). In attempting to concentrate the filtered solution by heat a heavy white precipitate, resembling in a measure barium sulphate in appearance, came down. The utmost care was necessary in boiling the solution as the bumping was often quite violent. The precipitate redissolved when the solution was cooled. In evaporating the solution on the water-bath the precipitate appeared and was dissolved again on cooling.

A thorium citrate is described by Chydenius[2] but he did not investigate it further than to determine the percentage of oxide present. The investigatin of this citrate, not previously noted, is well under way and will be published later as a separate paper. For our purposes here it suffices to state that the precipitate may best be obtained and separated by diluting the solution from five to ten times and holding it at or just below 100° C. This has been done by placing the large beaker (Jena glass) into a boiling water bath for an hour. The precipitate settled well and the clear supernatant liquid was decanted; the precipitate was washed several times with boiling water by decantation, the settling occurring while the beaker was surrounded by boiling water. Finally the precipitate was thrown upon a large filter-paper and washed several times with boiling water, or until the wash-water was only

1 All determinations here and elsewhere in this paper were corrected to 4° C.

2 Pogg. *Ann.*, 119, 55 (1863); "Kemisk undersökning of Thorzord och Thorsalter Helsingfoss, 1861.

faintly acid to litmus. The precipitate was carefully removed from the funnel, avoiding contamination with fibers of the filter-paper, and brought to a constant weight at 105°C. in an air-bath. Prepared thus the body is a beautiful white heavy amorphous powder and is an hydrated citrate of the real thorium.

Portions of this purified citrate made at different times were ignited in platinum crucibles with blast, and the specific gravity of the oxides determined.

Oxide taken. Gram.	Specific gravity. corrected to 4° C.
0.1989	9.234
0.6000	9.253
0.3830	9.210
0.4166	9.188[1]

From these determinations it appears that Nordenskjöld and Chydenius very likely at one time had the nearly pure thorium compound. I am inclined to the opinion that the oxide obtained by me above is still not quite pure for reasons given below. (See also radio-active experiments.) One of the regrettable features of the paper is that I am unable yet to submit the results of the spectroscopic investigation of the material. Preliminary atomic weight determinations have been made from this oxide, however.

The filtrates (without the wash-water) obtained from the citrate mentioned above were concentrated in platinum on a water-bath. As the solution became concentrated a little more of the insoluble citrate separated out, but in one series of the experiments no effort was made to separate it, but the whole was carried down to a thick sirup and allowed to cool, when it became a mass of solid crystals, more or less opaque from the insoluble citrate bound up with the mass. Two grams of this material were ignited and the specific gravity of the oxide determined:

[1] Citrate prepared from second heating of one of the solutions which was not completely precipitated at first.

Oxide taken. Gram.	Specific Gravity.[1]
0.4000	10.50

A larger quantity of the saturated citrate solution was prepared and most of the insoluble citrate removed according to the method given. About 2 liters of filtrate (wash-water not included) were concentrated to 400 cc. in platinum on the water-bath when a crystalline scum began to form. The dish was covered and allowed to stand over night. A few heavy crystals separated at the bottom. The thick sirup was drained from the crystals which, without crushing, were then washed three times with water, and dried at 120° C. On ignition, 31.61 per cent. of oxide was obtained. The specific gravity of the oxide was determined.

Oxide taken. Gram.	Specific gravity.
0.1789	8.77
0.2024	8.47

What this oxide is I am unable to say, unless it be the new body recently reported by Hofman and Prandtl[2] as a contamination of zirconium in euxenite. It consitutes only a very small percentage of the thorium and demands careful investigation, which I cannot at present undertake on account of the wealth of other material demanding more immediate attention. I should like to have the privilege of investigating it later, however.

When the sirup obtained above was further evaporated to about 300 cc., a white crystalline body separated and formed a thick coating on the bottom of the dish. The liquid was decanted, and the crystals washed until the water was only faintly acid, and dried at 120° C. The residue amounted to 16.20 per cent. after ignition, and had a specific gravity of 10.14, using 0.3820 gram of oxide.

1 Mr. R. O. E. Davis, assistant in the laboratory, aided in some of the physical constant determinations. He is at present at work on the citrates and molybdates.

2 *Ber. d. chem. Ges., 34, 1064* (1901).

On continued concentration small crops of crystals were obtained consisting primarily of citric acid with decreasing percentages of oxide. These salts have not yet been closely studied. When the sirup was brought to about 200 cc. it was diluted approximately to a liter and boiled. A small precipitate very similar to the first insoluble thorium citrate, yet different, was obtained. The oxide obtained when the material was ignited was exceedingly white.

Oxide taken. Gram.	Specific gravity.
0.1812	11.26

As the quantity of the material obtained was very small, too much weight should not be given to this value.

Two portions of the filtrate from this precipitate were evaporated to dryness in a platinum dish, ignited, and the specific gravity of the residue determined:

	Oxide taken. Gram.	Specific grayity.
I.	0.3560	10.46
II.	0.8316	10.53

II was strongly ignited in a covered platinum crucible for three hours.

These determinations prove the presence of an oxide having an unusually high specific gravity, which cannot be accounted for except by the presence of either a new oxide of a known element having greater density than the usual non-volative residue after ignition, or an unknown element. It is needless to say that the absence of such heavy substances as lead from the reagents was proved. From the variation in the values, assuming no error in manipulation, the oxide is not yet pure, but careful fractionation, using much greater quantities of the material, gives good promise.

II. EXPERIMENTS ON THE RADIO-ACTIVITY OF THE OXIDES.

In writing of the now well recognized Becquerel rays, M. and Mme. Curie[1] say that "the property of emitting rays***

[1] *Compt. rend., 127, 175; Chem. News, 78, 49* (1898).

which act on photographic plates is a *specific property of uranium and thorium.*" Sir William Crookes[1] has practically proved that the radio-activity of uranium is due to a constant constituent, which can be partially fractioned out, Ur(X). In the same paper Dr. Crookes presents the results obtained in a few preliminary experiments he made to separate thorium compounds into an active and inactive body.[2] His experiments in fractioning thorium sulphate gave negative results. However when he obtained six fractions by crystallizing the nitrate, "the oxide from the first end crystals gave a feeble action, while the other end gave an impression about three times as intense. This points to the possibility of separating from thorium its radio-active substance" (p. 421). My own experiments are in exact accord with the above. The oxide (sp. gr. 9.25) obtained from the insoluble citrate affects the sensitive plate in the dark after an exposure of seventy-two hours but slightly, while the oxides of higher specific gravity are quite active. A number of plates have been exposed, using oxides obtained through the research, monazite sand from which the thorium salts were prepared, uranium nitrate, acetate, uraninite, and blanks for comparison. The radio-activity increased with the increase in specific gravity. For reasons given below I am of the opinion that the 9.25 thorium oxide is not quite pure, that is, free from traces of the higher oxide, hence its faint activity. (See above. Method of application is outlined below.)

I am not yet ready to assert that the new substance obtained is not the third radio-active body reported by Debierne in pitchblende,[3] actinium, which he states, belongs to the iron group. From Madame Curie's statement, Debierne supposes that the radio-active property observed in thorium compounds does not belong to this element, but is due to a foreign material, hence actinium (?). From Rutherford's experiments

[1] *Proc. Roy. Soc.*, *66*, *409*.

[2] *Loc. cit.*

[3] *Compt. rend.*, October 10, 1890, and April 2, 1900; *Chem. News*, *81*, *169*.

on induced radio-activity, one is loath to accept the radio-activity of unprotected bodies as sufficient evidence of their sameness. I have not so far had time to apply the radiant matter test, but amassing chemical evidence so far obtained points to the presence of a hitherto unrecognized body.

An account of the method used in these preliminary experiments on the radio-activity of thorium and its constituents may be of interest. The plan was essentially the same followed by Dr. Crookes,[1] differing somewhat in details. Placing small circular pill boxes containing the materials directly on the same sensitive plates was not satisfactory on account of the excessive radiation from the concentrated active body in all directions. Black glazed paper, the size of the plate, was punctured with circular holes about 1.5 cm. in diameter and placed dark side up on the plate. A sheet of silver-free lead, about 0.5 mm. thick, was similarly cut and placed on the paper, which served to protect the plate. The material was placed in quantities varying from 0.25 to 1 gram in small exhibition glass tubes 1 cm. in diameter and 5 cm. tall. These cells were closed by sealing thin circular microscope slide covers to the flange with Canada balsam. After air-drying, the cells were inverted and the sealed end placed neatly over the circular openings in the lead and paper, thus exposing portions of the plate to the radiant action downward through a thin medium of glass and air, as the cells were not in contact with the sensitive surface nearest the tubes being held up by the flange, which projected beyond the circular opening. To eliminate lateral radiant action, each cell was then surrounded by a cylinder of lead, which was filed to fit snugly upon the sheet lead below. These cylinders were about 2.5 cm. in diameter, inside, and 5.25 cm. high. Such a battery, having from two to eight cells differently charged, was placed in a box, closed, covered with black glazed paper, several thicknesses of cloth and locked in a dark room for various lengths of time, 24 to 145 hours. The plates were afterward developed.

[1] *Loc. cit.*

III. DETERMINATION OF THE ATOMIC WEIGHT OF THORIUM.

As this is a preliminary paper, a detailed discussion of the various atomic weights accorded thorium by the several workers is beyond its scope and will be reserved for a subsequent communication. Suffice it to say the compounds made use of, as reported by Clark,[1] *viz.*, the sulphate, oxalate, acetate, and formate, offer little promise of either concordant or satisfactory results. Brauner and Povlicek[2] have recently called attention to a serious source of error in using the anhydrous sulphate. The careful work of Brauner on the heptadrated thorium tetrammonium oxalate[3] gives good results for that substance, but in atomic weight work it is desirable to have as few factors as possible for consideration. It is a matter for surprise that none of the halogen compounds have ever been used. The tetrachloride was selected for this preliminary work. It may be that the bromide will yield even better results.

Preparation of Thorium Tetrachloride.—Thorium dioxide was prepared from the purest insoluble citrate by intense ignition, ground to an impalpable powder in an agate mortar and an intimate mixture made with thick paste composed of corn starch and pure sucrose syrup. Balls, 5–8 mm. in diameter, were made from this, dried and baked at 140–150° C. in a platinum milk pan until thoroughly browned. They were then heated in a closed platinum crucible with a Bunsen burner until thoroughly carbonized. About a dozen of these black pellets were placed into a perfectlyclean dry combustion tube. Freshly prepared, pure dry chlorine was passed through the tube, that portion immediately surrounding the balls being heated to dull redness, At first a white vapor formed; some settled on the tube quite a distance from the heat and some was swept into the lime absorbtion tower by the chlorine, In

[1] Smithsonian Institution, Constants of Nature, V, revised 1897, 204.
[2] *Chem. Soc. (Lond.)* Proc. XVII, 63—1901.
[3] *Chem. Soc. (Lond.)* Trans. 73, 951—1898.

Chydenius' paper it appears that Berzelius observed this "weisser dampf" and he states that it is not finely divided thorium chloride. This is the impurity which was noted above. Then beautiful fern-like crystals, only slightly volatile, began to form immediately over and on the balls. These crystals are the purest compound of thorium ever prepared in this laboratory.[2] After two hours the heat was removed and the tube allowed to cool in a current of chlorine, which was subsequently removed by pure dry air free from carbon dioxide.

The crystals absorbed water and were quite soluble. The white volatile vapor mentioned was even more deliquescent. The fernoid crystals were dissolved in water, the solution made up to 100cc. in a standard flask, and aliquot portions measured out by means of a calibrated standard burette, whose outlet was so constricted as to deliver 0.01 cc. by drops.

Those portions taken for the determination of thorium were measured directly into weighed platinum crucibles, which were placed into perforations of a porcelain plate over a water bath, and evaporated to dryness. The gelatinous oxychloride was gently heated first over a Bunsen burner and then ignited to a constant weight over the blast lamp. A beautiful white glistening residue of thorium dioxide was obtained.

For the determination of chlorine, measured quantities were taken, diluted to 75cc., and acidulated with 1 to 2 drops of pure nitric acid. Just below the boiling point the chlorine was precipitated with a weighed quantity of silver nitrate prepared according to Stas. The precipitate was caught in a weighed Gooch crucible, the suction flask being placed in an asphalted box. The crucible and silver chloride were then dried in a dark air-dath at 140°–150° C. to a constant weight. The acid-washed asbestos from which the felt was made was

[1] *Loc. cit.*

[2] I was assisted in the preparation of the tetrachloride and the absolute ether by Dr. A. S. Wheeler, associate professor, to whom I wish to express thanks.

previously digested in boiling hydrochloric acid, then water, then hot nitric acid, and finally washed with boiling water until not the faintest evidence of the presence of halogens was obtained.

The following are the results obtained:

	Taken.	Thorium dioxide found	Per 100 cc.
A.	25 cc.	0.0903	0.3612
		Silver chloride found.	Cl per 100 cc.
	10 cc.	0.0812	0.2007
		Thorium dioxide found.	Per 100 cc.
B.	15 cc.	0.0542	0.36133
		Silver chloride found.	Cl per 100 cc.
	15 cc.	0.1220	0.20105

Calculations:

A. $\frac{XO_2}{Cl_4} = \frac{0.3612}{0.2007} \quad \therefore X = 223.2$

B. $\frac{XO_2}{Cl_4} = \frac{0.36133}{0.201056} \quad \therefore X = 223.3$

} Atomic weight of thorium.

It is very interesting to note that both Hermann's[1] and Delafontaine's[2] results obtained from $2ThSO_4 . 9H_2O$ and corrected by the observations of Hillebrand[3] to $ThSO_4 . 4H_2O$ give 223,06 $\pm$ 3426. On account of the doubt as to the composition of the sulphate and the wide divergence in the value obtained from the accepted atomic weight of thorium, Clarke correctly threw it out of consideration. From the preliminary values obtained above, which were not reduced to a vacuum; the results assume importance.

As the tetrachloride is so readily decomposed by water and a direct comparison between a known amount of the tetrachloride and the oxide obtained therefrom is desirable, a complete analysis of the body was made.

Preparation of Pure Anhydrous Ether.—Ether, which had stood over calcium chloride for a year, was decanted over fresh fused calcium chloride and allowed to remain a week. It was then distilled and placed over freshly cut sodium and

[1] Constants of Nature, Clarke, Part 5, revised, 1897, 204.
[2] *Arch. sci. phys. et not.*, (2), **18**, 343.
[3] Bulletin 90, U. S. Geological Survey, 29.

allowed to stand four days. It was again distilled and placed over fresh sodium and left three days until no more bubbles of hydrogen escaped. This process was repeated until fresh sheets of sodium showed no tarnishing and no hydrogen bubbles were observable. It was finally distilled. In all these operations special precautions were taken to prevent the absorption of a trace of moisture.

More tetrachloride was prepared and that part of the tube on each side and just above the pellets was placed in a perfectly dry Soxhlet apparatus. At the upper end of the reflux condenser was attached a calcium chloride tube. After the apparatus was in place it was learned that the ground glass connection of the condenser was not air-tight. A selected velvet cork was substituted. When the extraction had continued about six hours, it was discovered that an overlooked small defect of the cork had permitted the gradual introduction of about a drop of water, which came from the sweating of the condenser overhead. As this vitiated the experiment, the ether was evaporated and the whole dissolved in water. During the evaporation a small amount of hydrochloric acid was detected in the vapor. For that reason the expreriment must be discarded, but the results are given:

C. { Thorium dioxide found..... 0.1020
Chlorine found..... 0.05636

whence

$$\frac{XO_2}{Cl_4} = \frac{0.102}{0.05536} \quad \therefore 224.65 = \text{atomic weight.}^1$$

The pellets, which were covered with excrescences of crystals of the tetrachloride, were repeatedly shaken in a small Erlenmeyer flask with about 10cc. of pure dry ether. The ether was filtered directly into a weighed platinum crucible, which was placed in a vacuum desiccator, in the bottom of which was pure concentrated sulphuric acid and above chipped paraffin. The tetrachloride appears to be soluble in about 1000 parts of dry ether. Proper precautions were taken to

[1] Higher chlorine value decreases the atomic Weight of thorium.

dry the air used to relieve the vacuum of the desiccator and prevent back rush of moist air from the pump. The crucible was dried at 105°C. for half an hour in an air-bath already heated and weighed. The finely crystallized tetrachloride was dissolved in 2 cc. of pure distilled water to decompose the chloride and form the oxychloride, evaporated to drynesa, ignited and weighed. The following results were obtained:

Tetrachloride used..... 0.0822 gram.
Dioxide found..... 0.0575 gram.

$$\text{Hence } \frac{XO_2}{XCl_4} = \frac{0.0574}{0.0822}. \quad \therefore 222.13 = \text{atomic weight.}$$

In all calculations the following values were used: O=16, Cl=35.45, and Ag. = 107.93.

Another ether extract was made as above, weighed and dissolved in water and the chlorine determined by titration with a standard silver nitrate solution, using potassium chromate as indicator,—method of Pelouze. Tetrachloride used, 0.01 gram; cubic centimeter of silver nitrate required, 3.9, each cubic centimeter being equivalent to 0.001 gram chlorine; hence 0.0039 gram chlorine or 39 per cent. The percentage of the oxide obtained from the chloride, 69.83.

	Calculating for $ThCl_4$ using 222.	using 223.3.	Found.
Th	61.03	61.18	
or,			
ThO_2	69.83	70.17	69.83
Cl_4	38.97	38.84	59.00

These discrepancies do not deserve discussion as the data are far too few for ascribing the proper atomic weight to thorium. The last analysis is important; however, as we have secured a substance of known composition, which may be prepared pure and which lends itself for atomic weight determinations, as the dual constituents, thorium and chlorine, can be determined with accuracy. The figures hold interest however, as it may be asserted that the real mass equivalent of thorium is much below that hitherto ascribed to it. It is of greater interest to attribute the old values to a constant un-

known impurity in practically all the materials used. This constituent must be an element of much higher atomic weight.

With this evidence of the complexity of thorium the problem now engrossing my personal attention is the separation of the compounds of this element, the proof of their purity and determination of the physical constants and chemical properties. From insufficient data already obtained, in case the element be tetravalent, it appears that the atomic weight lies detween 260 and 280. On account of the extensive occurrence, in this state (North Carolina), of the monazite sands from which the original material was obtoined, if the investigation give a successful issue, I should like to have the element known as *Carolinium*, with the symbol *Cn*.

As this is a preliminary paper only, it may not be out of place to state the lines of research bearing immediately upon the subject that are already under way in this laboratory.

1 The preparation of an adequate quantity of perfectly pure thorium compounds with which to continue the study of the radio-activity, the spectrum, and to obtain sufficient tetrahalides for the determination of the true atomic weight of that element, which is assuredly different from the number usually accorded it and dependent at present upon evidence not wholly satisfactory.

2. An investigation of several of the old thorium compounds, like the hydrated sulphates, citrates, etc., and determination of their composition.

3. An investigation of the volatile chloride obtained in the preparation of the thorium tetrachloride.

NEW EAST AMERICAN THORUS.

CONTRIBUTIONS FROM MY HERBARIUM, NO. XIII.[1]

W. W. ASHE.

CRATAEGUS DECORA. A small tree 3-5 m. in height, with a small oval crown formed of short ascending branches; or generally a bushy shrub, branching near the ground. Bark on the trunk dark gray and scaly, sparingly armed, that on the branches smoother and lighter. Twigs at first sparingly pubescent, soon glabrate, very slender, geniculate, dull chesnut-brown, armed with slender 3-4 cm.-long thorns. Leaves glabrate below, at first oppressed pubescent above, ovate, 3-5 cm. long, 2-4 cm. wide, acute at apex, rounded or broadly cuneate at base, 2-4 pairs of short lobes, sharply serrate above. The flowers, which appear from May 25, to June 5, when the leaves are about two-thirds grown in simple glabrous 3-5-flowered cymes, are cup-shaped 16-18 mm. wide and on erect pedicels, brachate with numerous oblong bright red pectinately glandular caducous bractlets; calyx cup shaped, very broad at top, the disk 6-7 mm. wide, the lobes oblong from a broad base, sharply glandular serrate, soon reflexed. The fruit, ripening and falling by the middle of October, with and just after the leaves, is globose, 13 mm. thick, dark red with small spots of green and russet, and capped by the obtuse serrate reflexed lobes, borne on the projecting tube; flesh greenish-yellow, firm, bitterish; seed generally 4, thick and coarse, grooved on the back 7 mm. long.

CRATAEGUS CRUX A small bushy tree, sometimes 7m. in height, with dark gray scaly bark on the armed trunk, and brown smooth bark on the long branches. Twigs stout, glabrous, geniculate, glossy brown-purple, armed with very numerous 5-7 m. long, stout purple-brown thorns. Leaves

[1]Issued March 1, 1902.

thick, dark green and pubescent above, glabrous beneath, broadly ovate or nearly orbicular, 4-8 cm. long, sharply serrate. The flowers appearing the first week in June in large 15-25-flowered, pubescent corymbs, are about 18 mm. wide; stamens 10; anthers large, white; calyx large, pubescent, the lobes lanceolate, deeply laciliate, glandular, pubescent, reflexed after anthesis. The fruit which ripens in October and falls with the leaves or withers, turning black, on the tree, is subglobose 13 mm. thick, bright scarlet, wax like, capped by the broad reflexed nearly sessile lobes; flesh soft pulpy, orange, sweet; seed 2 hemispherical, 7 mm, long, grooved on the faces.

The species above proposed is related to *C. neo-fluiralis* Ashe (Jr. E. M. Sci. Soc. XVI, II, 71) from which it is separated by having only 10 stamens, white anthers, and larger more orbicular foliage. The two plants grow together along the New River, Ashe County, N. C.

CRATAEGUS LENTA. A slender tree 5-8 m. in height with short spreading or ascending branches forming an oval crown; the bark on the unarmed trunk dark brown and shallow-furred, that on the branches gray-brown and smooth. Twigs slender, first puberulent, bright chesnut-brown, sparingly armed with slender 3 cm. long thorns. Leaves thin, bright green, at first sparingly pubescent below on the veins, but soon glabrate, oppressed pubescent and rough above with short hairs, ovate, 6-7 cm. long, 4-5 cm. wide, taper-pointed, cuneate at base, shaply serrate, 3-4 pairs of short lobes with acute reflexed tips, lower pair of primary veins arcuate; petiole slender, 2-3 cm. long. The flowers, borne in compound 8-12-flowered cymes on ascending pubescent pedicels, are cup shaped, about 17 mm. wide, and appear early in June; calyx puberulent, the long lanceolate lobes serrate above the middle, spreading after anthesis; stamens 5-10, anthers rose-purple; bractlets large, bright purple. The fruit, borne in small clusters, is pyriform, 18 mm. long, 14 mm. wide, scarlet, capped by the slender lobes; ripening early in October and falling after the leaves; cavity narrow; flesh soft, mealy, orange,

seed 3-4, apical, about 7 mm. long, 3 mm. across the slightly furrowed back, lateral faces plane.

At Port Huron, Mich., where the type material was collected by C. K. Dodge and W. W. Ashe, this handsome tree is not uncommon. It is sepreated from *C. villipes* Ashe by the more pyriform fruit, shorter pedicels, and smaller foliage.

CRATAEGUS RHODELLA A slender shrub, exceptionally 3m. in height, with dark, nearly black, scaly bark, and short horizontal branches. Twigs slender, at first pubescent, at length nearly glabrous, armed with numerous slender 4 cm. long thorns. Leaves thick, dark green and at first appressed pubescent above, paler and soft pubescent beneath, rhombic, ovate, 4–6 cm. long, 3–5 cm. wide, acute at apex, cuneate at base, sharply serrate above, and somewhat lobed; petiole short and stout. The flowers, which appear about the first of June, in 3–6-flowered small simple villose cymes, are about 18 mm. and on 2–3cm-long pedicels; calyx small cup-shaped, pubescent, the lanceolate serrate, pubescent lobes spreading after anthesis; stamens 20 large, anthers large, rose-purple or dark. The fruit, which ripens late in September and largely persists until November, in small clustres, is pyriform, about 14 mm. long, not quite so thick, orange or with red cheeks, pubescent and capped by the reflex green lobes; flesh firm, pale yellow or white, sweet, juicy; seed 3-5, 6-7 mm. long, thick and coarsely ridged on the back, lateral faces plane.

C. rhodella is related to *C. uniflora*; but from this, and the other related species with which it occurs, it can be separated by the larger flowers and rose-colored anthers. It is common along streams in the basin of the Little Tennessee River. The type material is from near Franklin, on the Cullasagee river.

CRATAEGUS TORTILIS A small tree 4–8 m. in height with spreading branches forming an oval crown; bark on the tree dark gray and scaly, that on the branches gray and smoother. Twigs slender, glabrous, chestnut-brown, sparingly armed with short 3–4 cm. long thorns. Leaves dark

green, thick and firm, glabrous, ovate 5–7 cm. long, 3.5–5 cm. wide, taper pointed, rounded or broadly cuneate at base, finely and sharply serrate, 3–4 pairs of short ascending lobes; petiole slender, 2–3 cm. long. The flowers which appear early in June in large compound glabrate corymbs, are saucer-shaped, about 20 mm. wide; calyx obconic, glabrous, the narrowly triangular glandular-serrate lobes nearly as long as the petals, spreading after anthesis; stamens normally 20, filaments very large persistent, coloring scarlet. The fruit, ripening about the middle of October and persistent until after the leaves fall, borne in large, wide-spreading, 10–15-fruited drooping corymbs, is subglobose, often slightly tapering at apex, about 1 cm. thick, bright deep red, wreathed by the narrowly triangular, keeled, dark red, ascending lobes; seed generally 5, small, 5 mm. long, lateral faces plane, flesh orange, firm and juicy, cavity large.

C. tortilis may be regarded as the type of a new group, to which *C. McGeeae* proposed below, also belongs. This type material was collected near Milwaukee, Wis., by Dr. Lewis Sherman.

CRATAEGUS MCGEEAE A small tree 4–6 m. in height with ascending or spreading branches, the bark on the trunk dark gray, broken into small scales, that on the branches light and smooth. Twigs slender, at first pubescent, at length glabrate, chestnut or olevacious, sparingly armed. Leaves bright green, membranacious, pubescent and rough above with short hairs, glabrous and pale beneath, ovate, 6–8 cm. long, 3–5 cm. wide, acuminate at apex, cuneate or rounded at base, sharply serrate, 3–5 pairs of short notches above the middle; petiole slender, about 2 cm. long, winged above, puberulent at the red base. The flowers which appear the last of May in large compound pubescent corymbs, are about 19 mm. wide; calyx cup-shaped, the lobes narrowly triangular, serrate, spreading after anthesis. The fruit, borne in large compound clusters, is globose, about 9 mm. thick, bright scarlet, capped by the elongated serrulate spreading lobes, ripening late in September and persisting until after the leaves fall; flesh yellow,

thick, juicy; seed 2–3, small, about 5 mm. long, slightly grooved on the rounded back, the lateral faces plane.

Open woods and fields, southeastern Iowa, where collected by Miss Emma McGee.

CRATAEGUS TENAX A tree 7–10 m. in height, with a short bole 2–4 m. in length and seldom more than 2 m. in thickness, and long horizontal branches forming a glabose or oval crown; bark on the trunk ash-gray or darker, broken into oblong, rather thick firm scales, and armed with numerous long, compound, gray thorns; bark on the branches paler and smooth. Twigs glabrous, nearly straight, glossy red-brown, armed with long slender, 6–8 cm. long ascending thorns. Leaves glabrous, thick and lucid, dark green above, paler beneath, ovate or oblong, 5–6 cm. long, about 3 cm. wide, rounded or acute at the apex, cuneate at the entire base, finely and obtusely serrate about the middle (or on vigorous shoots the leaves 7–10 cm. long and coarsely and irregularly serrate); petiole very short. The flowers, which appear about the middle of June in large compound glabrous corymbs, are about 22 mm. wide and saucer-shaped; calyx small, the narrow, acute, entire lobes spreading after anthesis; stamens about 16, anthers rose-purple or darker. The fruit, borne in large compound spreading clusters on pendent pedicels, is subglobose, 14–18 mm. long, scarlet or mottled with yellow and olive, capped by the reflexed lobes; cavity shallow, 3–4 mm. wide; flesh pale yellow, firm and juicy, acid; seed 2, 9-11 mm. long. The fruit ripens in September or October and falls after the leaves.

C. tenax is one of the most common thorns in the vicinity of Port Huron, Mich., where the type material was collected by C. K. Dodge and W. W. Ashe. It is separated from the other cockspur thorns of this region by the larger fruit and folige, more numerous stamens and darker anthers.

CRATAEGUS GLARIOSA A small tree 2–5 m. in height, with few long horizontal branches forming an open flat-topped crown, the bark on the slender trunk scaly and nearly black,

that on the branches lighter. Twigs slender, flexuous glabrate, dark brown-purple, armed with numerous glossy brown-purple short, 2-3 cm. long, thorns. Leaves thick, dark green and soon glabrous above, paler and somewhat pubescent beneath, especially along the veins, broadly oval or nearly orbicular, 5–8 cm. long, nearly as wide, abruptly acute at the apex, rounded to subcordate at base, sharply and coarsely serrate, standing erect on the 2 cm. long glandular glabrous petiole. The flowers, which appear about the middle of June, are in large compound, pubescent corymbs; stamens small 10; calyx cup-shape, the lanceolate pubescent, lacineate lobes, spreading after anthesis. The fruit, which ripens early in October and falls after the leaves, is globose, about 15 mm. thick, bright scarlet, capped by the brown spreading lobes, is in large compound clusters; flesh thin, yellow, soft, very sweet; seed generally 4, somewhat grooved on the back, lateral faces plane.

This plant forms thick clumps on the sandy shores of Lake St. Clair, Michigan, where the type material was collected by C. K. Dodge and W. W. Ache. In habit and the large, round, erect leaves, it closly resembles *C. Michiganeasis*, which goes with it.

CRATAEGUS AMARA A small tree 4–6 m. in height with long spreading or ascending branches forming a rather open, globose crown; the bark on the generally unarmed trunk dark gray, broken into small scales, that on the branches smoother and lighter. Twigs slender, glabrose, purple-brown, armed with numerous 3–4 cm. long thorns. Leaves subcoriaceous, glabrous dark green, lucid, spothulate, 5–7 cm. long, 2–3 cm. wide, coarsely serrate and lobed above the middle, entire at the cuneate base. The flowers, which appear from May 20th to June 4th, in 6–12-flowered nearly simple glabrous cymes, are cup-shaped, about 16 mm. wide, and on ascending pedicels; calyx small, the lobes acuminate entire or serrate at apex, reflexed after anthesis; stamens 10, small, anthers pink. The fruit, borne in slightly compound clusters on long drooping pedicels, ripening and falling late in October, after the

leaves, is slightly oblong, 12–14 mm. long, full and rounded at the apex, elliptic or 3-angled in cross-section, lemon yellow, capped by the small reflexed lobes, the tube slightly projecting; flesh hard, white, bitter; seed 2, apical.

Crataegus amara with its long narrow spreading leaves is a very characteristic and distinct tree, especially when covered with the bright yellow fruit. It is common in Ashe county, N. C., along the New River, where the type was collected at Elk Cross Roads. It is related to *C. viminea*, proposed below, and forms the type of a new section of the genus.

CRATAEGUS VIMINEA Sometimes a small bushy tree 5 m. in height, but generally a shrub with several stems together, the short branches ascending. Twigs long and slender, red-brown, glabrous, armed with numerous 4 cm. long thorns. Leaves glabrous, sub-coriaceous, dark green, lucid, broadly spathulate, 4–5 cm. long, 2–3 cm. wide, rounded at the lobe and cuneate apex, entire at the cuneate base. The flowers, which appear the last of May and the first week in June, in nearly simple 4–6-flowered glabrous cymes, are about 15 mm. wide, and on short erect pedicels; stamens 10, anthers white, calyx cup-shaped, the lobes entire, short from a broad base, obtuse, reflexed after anthesis. The fruit, which ripens in October and falls after the leaves, is slightly oblong, about 11 mm. long, dull light scarlet or orange, mottled freely with green and russet, capped by the large projecting calyx-tube, the lobes, if persistent, reflexed; flesh thin, hard, dry, bitterish, greenish-white; seed generally 2, 8 mm. long, thick, somewhat grooved on the back, lateral faces plane; cavity broad, shallow, obconic.

C. viminea is evidently related to *C. amara*, proposed above, from which it is separated by the smaller flowers, and foliage, smaller inflorescence, and different fruit. It forms thickets along roadsides and in meadows, on Buffalo creek, Ashe county, N. C.

CRATAEGUS PASCENS. A tree 7–10 m. in height with numerous ascending or spreading branches forming an oval crown,

and a thorny trunk often 2 dm. thick, the bark on the trunk dark gray-brown and scaly, but close, dark gray and smoother on the branches. Twigs stout, chestnut-brown, shining, glabrous, armed with numerous 3-4 cm. long ascending thorns. Leaves membranaceous, bright green, glabrous, oval or broadly oval, ample, 4-7 cm. long, 4-6 cm. wide, rounded or subcordate at base, acute at apex, with 3-4 very shallow notches above the middle, sharply serrate, remaining bright green until late in October; petiole slender, 3-4 cm. long. The large, 18-20 mm. wide flowers appear in June in large compound glabrous corymbs; calyx obconic, glabrous, the very narrow serrulate lobes reflexed after anthesis; stamens 5-8. The fruit, borne in large compound wide-spreading clusters, on long pendent pedicels, is subglobose or slightly oblong, about 18 mm. thick, scarlet, capped by the sessile linear spreading lobes with ascending tips, ripens early in October and falls with and after the foliage; flesh thick, sweet and mealy, seed generally 4, 6-7 mm. long, very narrow across the back, apical.

Collected at Port Huron, Mich., where it is not uncommon by C. K. Dodge and W. W. Ashe; and at Milwaukee, Wis., by Dr. Lewis Sherman. From *C. Holmesiana* and the other glabrous species of this group now reconized, *C. pascens* may be separated by the larger and thicker fruit borne in more ample clusters.

CRATAEGUS CAESA A small tree 6–10 m. in height with a slender trunk 2–4 m. long and seldom more than 1.5 dm. thick and slender ascending branches forming an oblong or oval crown; the bark on the unarmed trunk dark brown and shallow-furrowed, that on the branches dark gray and smooth. Twigs slender, glabrous, or at first pubescent, chestnut brown, armed with very few short, 2–3 cm. long, rather stout spreading thorns. Leaves thin, bright green, at first pubescent on both sides, soon glabrate above, sparingly pubescent beneath even when old, ovate, abruptly acute at the apex, rounded or truncate at the base, 4–7 cm. long, 4–5 cm. wide,

with 5–7 pairs of short sharp notches, the lowest near the base, sharply doubly and coarsely serrate; petiole glabrate, 1.5–2 cm. long. The flowers which appear the last of May in small nearly simple cymes, are about 18 mm. wide, and borne in erect, pubescent pedicels; calyx obconic, the lobes narrowly triangular, serrate above the middle, appressed pubescent above, spreading after anthesis; stamens generally 5–8. The fruit, borne in 2–4-fruited clusters, or solitary, on short 15–3 cm. long spreading pedicels, is subglobose or oblong, 14 mm. long, 12 mm. thick, bright scarlet, capped by the persistent lobes, the tips ascending from a spreading base, the edges involute at base and coloring with the fruit; tube projecting in a short collar; seed generally 4, 7–8 mm. long, grooved on the rounded back, lateral faces plane.

C. caesa has been collected at Port Huron, Mich., by C. K. Dodge and W. W. Ashe, where it is found growing in the sandy soil, on the edge of woods skirting Lake St. Clair, but is not common. It is related to *C. anomala* Sarg. (Rhod. 3:74), from which it is separated by the differently shaped leaves, with rounder base, smaller oblong fruit, and nearly unarmed straight twigs.

CRATAEGUS CERNUA. A tree 7–10 m. in height with numerous spreading branches forming an oval crown, bark on the trunk gray-brown and scaly, unarmed; that on the branches gray and smoother. Twigs stout, orange or red-brown, glabrous, sparingly armed with rather stout, 4–6 cm. long chestnut thorns. Leaves membraceous, on unfolding rough above with appressed hairs, soon glabrous, glabrous below, ovate, 5–8 cm. long, 4–6 cm. wide, acute at apex, rounded or cordate at base; petiole slender, about 3 cm. long, pubescent. The flowers, borne in many flowered glabrate corymbs, which appear the last of May or early in June, are about 20 mm. wide; stamens 5, sometimes 10, anthers rose-purple or darker; calyx glabrous, the long narrow lobes serrate. The fruit, ripening late in September and falling early in October with or after the leaves, in nearly simple clusters,

on nodding 2–5 cm. long pedicels, is oblong, 17–20 mm. long, 14–13 mm. thick, crimson, capped by the elongated, erect lobes; flesh thick, orange; cavity large and deep; seed 3–4, large, grooved on the back.

From *C. Holmesiana* Ashe (Mitch. Journ. 16:2:78), to which it is closely related, it is separated by the different foliage, late flowering, larger and more glabular fruit, and more slender filaments. The type material was collected by Dr. Lewis Sherman, near Milwaukee, Wis.

CRATAEGUS AMICTA. A tree 5–6 m. in height, or sometimes shrubby, with gray scaly bark on the trunk, and smooth gray bark on the long ascending branches. Twigs slender, chestnut-brown, armed with stout 3–4 cm. long thorns. Leaves membraneous, at first pubescent above with short hairs, soon glabrate, nearly glabrous below, ovate or oblong, acute at apex, acute or rounded at base, 5–7 cm. long, 2–3 cm. wide, 3–4 pairs of short lobes, sharply serrate; petiole 2–3 cm. long, at first pubescent, soon glabrous. The flowers which appear early in June in large showy, many-flowered villose corymbs, are 20 mm. wide; bractlets few, greenish, soon deciduous; calyx glabrate, the lanceolate pubescent lobes serrate, spreading after anthesis; stamens 5–8. The fruit, ripening late in September and persisting until after the leaves fall, borne in large simple clusters on long drooping, nearly or quite glabrous pedicels, is oblong, about 13 mm. long and 11 mm. thick, crimson, capped by the lobes, the tips of which ascend from a spreading base; flesh soft, orange; seed 3–5, grooved on the back; cavity small, very shallow.

C. amicta occurs in northern Illinois, where it has been collected by Mr. H. C. Skeels, of Chicago, Ill., and W. W. Ashe. It is probably most closely related to *C. lobulata* Sarg. (Rhod. 3:12).

I find that the specific name *stropurpurea*, which I applied to a Southern Appalachian *Crataegus* (Mitch. Jour. —:—1901) has already been used (Stew. ex Nyman Conspec, 244, 1878) in this genus, and I therefore propose the name VELATA for this species.

The name *densiflora*, which has been used by Prof. C. S. Sargent (Rhod. 3:75, 1901) for a Canadian thorn has also been used before (Desf. ex Koch Dendrol. 1:186) in the genus *Crataegus*, and while the plant to which it was applied is not a *Crataegus* at all, it yet invalidates the name of the Canadian plant, for which I propose CRATAEGUS RUPESTRIS.

Also in *Crataegus Columbiana* Sarg. (Bot. Gaz. 31:229, 1901), which is a Texas plant, there is a duplication of the combination which Howell (Fl. N. W. America 1:fas. 2:163, 1884) recently applied to a Pacific coast tree. I would suggest for the Taxas plant the name C. QUERCINA, in allusion to its association with the oak forests of the Brazos river.

CRATAEGUS VITELLINA. A small tree 5-7 m. in height with numerous spreading branches, forming a compact globose crown, the bark on the slender armed trunk dark gray-brown and broken into small scales, that on the branches gray and smoother. Twigs slender, glabrous, nearly straight, sparingly armed. Leaves membraceous, glabrous, dark green above, paler benath, obovate, 3-5 cm. long, 2-4 cm. wide, rounded or obtuse at the apex, cuneate at the entire base, obtusely serrate above the middle, and with a few shallow notches. The flowers, which appear about the middle of May in small, 5-7-flowered glabrose cymes, are 15-16 mm. wide, and deeply cup-shaped; calyx glabrous, cup-shaped, the lobes short and broad, nearly entire, reflexed after anthesis; stamens 20, filaments erect, anthers dark rose-purple. The fruit, borne in small clusters on spreading pedicels, ripening early in October and falling with or soon after the leaves, is globose, about 1 cm. thick, bright yellow, capped by the projecting collar of the broad calyx, and the short reflexed lobes; flesh nearly white, mealy; seed 3-4, 6-7 mm. long, somewhat grooved on the back. *C. vitellina* inhabits fertile soil along small streams or hollows in the mountains of North Carolina. The type material is from Madison county, from an elevation of 2000 feet. It is not a common tree.

CRATAEGUS TINCTORIA. A tree 5-8 m. in height with

numerous spreading branches, forming a globose or oval crown, and a thorny trunk 1-1.8 dm. thick; the bark on the trunk dark gray and scaly, that on the branches gray and smoother. Twigs rather stout, geniculate, brown-purple, armed with numerous 4-5 cm. long thorns. Leaves rather thick and firm, glabrous, dark green, broadly ovate or deltoid, 4-6 cm. long, about as wide, acute at apex, truncate or cordate at base, 2-3 pairs of short lobes, rather shaply serrate, except at base; petiole short and stout, 1-2.5 cm. long. The flowers borne in 4-8 flowered glabrous cymes, appearing about the middle of May, are very large, 21-24 mm. wide, and cup-shaped; calyx broad, cup-shaped, the broad, triangular, entire lobes spreading after anthesis; stamens 20, filaments large erect, antlers, rose-purple. The fruit, which ripens in October and falls often long after the leaves, is subglobose, somewhat thicker than long, about 13 mm. thick, dark red, often glaucous, and capped by the spreading or ascending lobes; flesh firm, juicy, bright red; seed 3-4, large and coarse; cavity short and broad.

Crataegus tinctoria does not seem to be common. It has so far been found only in Madison county, N. C., and Cocke county, Tenn., where it inhabits the fertile banks of small mountain streams, or rich soil in hollows, growing beneath the shade of other trees. It is most closely related to *C. haemacarpa*, from which, however, it is abundantly separated.

ARSENIC PENTACHLORIDE.

CHAS. BASKERVILLE AND H. H. BENNETT.

The non-existence of arsenic pentachloride has for a long time been regarded as remarkable, especially so when the analogues of that element having atomic weights below and above it, phosphorus and antimony, show pentavalence toward the halogens.

Hurtzig and Geuther[1] endeavored to prepare it by treating arsenious acid with phosphorus pentachloride. Mayerhofer[2] passed chlorine into arsenic trichloride at —10° C., removing the excess of chlorine by a stream of carbon dioxide, and failed to obtain the body. Janovsky[3] treated phosphorus pentachloride with arsenic trihydride at 0° C. with negative results. Dumas[4] thought he had arsenic pentachloride, but Capitaine[5] proved it to be a mixture of As_4O_6 and $AsCl_3$.

Weber having prepared $SbCl_5PCl_5$, Cronander[6] sought its analogue $AsCl_5PCl_5$, but only obtained $AsCl_3PCl_5$. Marignac[7] obtained AsF_5 as a double fluoride of potassium. Sloane[8] prepared AsI_5 and endeavored to secure the pentachloride by saturating arsenic trichloride with chlorine at 23° C. at ordinary pressure and obtained the ratio As : Cl :: 1 : 4.447. There was a gradual decrease in the ratio up to 24° C. when it became 1 : 4.08, then there was an abrupt change rapidly approaching 1 : 3. Such observations made the existence of As_2Cl_8 quite conceivable.

[1] *Ann. Chem. Pharm. 111*, 171.
[2] *Ann. Chem. Pharm. 158*, 326.
[3] *Ber. d. chem. Ges., 8*, 1636, (1875).
[4] *Ann. Chem.* (Liebig) *33*, 337.
[5] *Jour. Pharm., 25*, 524.
[6] *Ber. d. chem. Ges., 3*, 1466 (1873).
[7] *Ann. Chem.* (Liebig) *145*, 249.
[8] *Chem. News, 46*, 194 (1881).

Baeyer's pentahalogen compounds of arsenic in which one to four chlorine atoms have been replaced by alkyl radicals and Michaelis'[1] work with phenyl residues are well known. Recently the pentavalent organic arsenic compounds have become much augmented by the extensive work of Michaelis.[2]

The procedure of Sloane (*loc. cit.*) offered encouragement, provided the reaction should be carried out at a lower temperature. Chemically pure arsenic trichloride was prepared and redistilled from concentrated suphuric acid and its purity determined by analysis. About 5 cc. of the liquid were placed in a dry test-tube buried in solid carbon dioxide loosely packed in a Dewar bulb and dry chlorine led in. The crystalline trichloride (m. p. —18° C.) assumed a greenish yellow color and became liquid, which grew in bulk. Besson[3] showed that arsenic trichloride saturated with chlorine at zero does not solidify at —30° C. Davy also showed that it does not freeze at —29° C. when well saturated with chlorine. After a few minutes, the time varying with different experiments, the stream of gas was cut off and the excess of liquid chlorine removed by fractional distillation. Chlorine boils at —33.6° C. We verified this by completely boiling away several cubic centimeters of chlorine at —33° C. in other experiments. As a safeguard we allowed the temperature to rise to —31° C. The liquid was cooled again to —35° C. and samples were removed as the temperature rose by means of a small pipette chilled to the temperature of the refrigerating agent. These samples in one experiment were placed directly in water; in another it was deemed better to place them in a dilute sodium hydroxide solution. In the former case immediate solution occurred with those portions removed at temperatures below —25° C., while at those higher a white precipitate, evidently of arsenious oxide, formed, increasing in amount with elevation of temperature. The orthoarsenic acid was determined

[1] *Ber. d. chem. Ges.*, *8*, 1316 and *9*, 1566.
[2] *Ann. Chem.* (Liebig), *320*, 271 (1902).
[3] *Compt. rend.*, *109*, 940.

as magnesium pyroarsenate and chlorine as silver chloride. The filtrate from the magnesiumammoniumarsenate in the former was tested for the presence of arsenious compounds. None were found up to —25° C., when arsenious acid was found in traces increasing in amount with rise of temperature. The ratio between arsenic, as pentavalent and chlorine was 1 : 5 or $AsCl_5$. At —25° C. the ratio rose to 1 : 6. The loss of chlorine and consequent return to the trivalent condition became more and more marked, the higher the temperature.

The following analytical results were obtained for two temperatures in one experiment:

Temperature.	Amount Taken.	Chlorine Found. per cent.	Theoretical.	Ratio Obtained. As : Cl
—35° C.	.1796	69.93	70.26	1 : 4.93
—25° C.	.26675	73.21	——	1 : 5.78

Arsenic penta-chloride is readily soluble in carbon disulphide and absolute ether cooled to —30° C. From the latter, when chilled several degrees, it crystallizes in yellow prisms. It loses chlorine when heated above —28° C. On exposure to the air it fumes, evolving hydrochloric acid vapor and as the temperature rises forms crystals, most likely of the trichloride, which melt soon to the liquid state. A special preparation was made and sealed in a tube. The greenish-yellow liquid when cooled to —38° or —40° C. (we had no thermometer for determining this accurately) formed beautiful yellow crystals.

It is not regarded necessary to give our several unsuccessful preliminary experiments to secure the body for analysis. Suffice it to say that placing the body in a pipette or weighing bottle at the temperature of the air brought about its immediate decomposition to the original trichloride, chlorine being evolved.

April 15th, 1902.